



Controllable synthesis of carbon nanotubes via autothermal reforming of ethyl acetate

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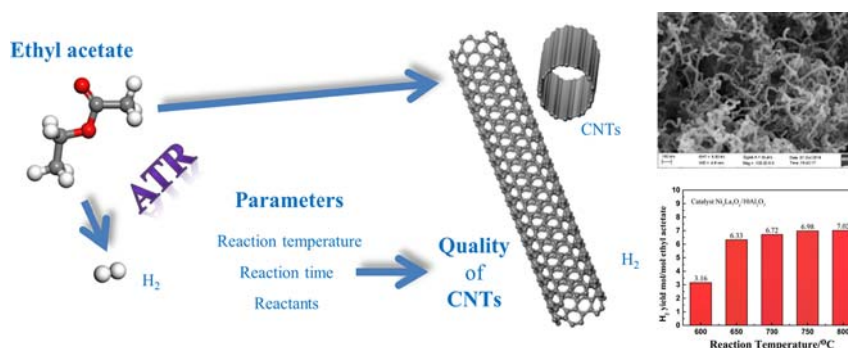
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HIGHLIGHTS

- New carbon sources ethyl acetate and waste cooking oil were applied for the synthesis of carbon nanotubes.
- Carbon nanotubes and H₂ were co-produced by autothermal reforming method.
- Reaction parameters such as reaction temperature, reaction time and reactants controlled the growth of carbon nanotubes.
- The “graphene-to-CNTs” mechanism was proposed to describe the growth of CNTs at low reaction temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Controllable synthesis of carbon nanotubes (CNTs) via autothermal reforming of ethyl acetate and waste cooking oil was studied for the first time. The products of the products were characterized by techniques of FESEM, XRD, HRTEM, Raman and XPS. Results revealed that reaction temperature, reaction time and reactants significantly affected the growth of CNTs. Ethyl acetate could be easily catalyzed into CNTs at 600 °C, which contained numerous defects and vacancies. High reaction temperatures led to the formation of CNTs with small diameter. The graphitization and purity of CNTs could be improved by increasing the reaction time. Besides, the amount of CNTs decreased by increasing the reaction time at low reaction temperature (<600 °C), whereas increased at high reaction temperature (700 and 800 °C). In addition, increasing the amount of O₂ and H₂O in reactants reduced the formation of irregular carbon species and promoted the synthesis of CNTs with ultra-small diameter. Two growth mechanisms for synthesizing CNTs from ethyl acetate via autothermal reforming were proposed: “tip-growth” mechanism and “graphene-to-CNTs” mechanism. Furthermore, the real waste cooking oil was also successfully catalyzed into CNTs.

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1. Introduction

Carbon nanotube (CNT as the abbreviation) is one of the most valuable one-dimensional materials, and its outstanding properties and applications have dramatically accelerated the development of the world [1–7]. Carbon source is a key part of the production of CNTs,

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because it not only provides carbon atoms for CNTs but also affects the growth and the morphology of CNTs [8–11]. Carbon sources such as methane [12], acetylene [13,14], benzene [15] and ethylene [13] are frequently-used. However, these carbon sources are valuable and required industrial raw materials in many fields. Herein, with the aim to satisfy the industrial demand of CNTs, it is of great significance to develop new carbon sources with the advantages of effective, abundant and resource-saving, or to design new approaches for controllable synthesis of CNTs.

The synthetic methods exhibit significant effects on the growth and the morphology of CNTs. Chemical vapor deposition (CVD) is the most potential method for the synthesis of CNTs [8,16], because of its outstanding advantages such as the easiest for industrial production, long length and quite pure CNTs, and low cost [3,17]. The reaction temperature is one of the main factors on controlling the growth of CNTs produced via CVD. Endo et al. [18] firstly produced the curved multi-walled CNTs (MWCNTs) from benzene at the temperature of 1100 °C using the iron nanoparticles, while José-Yacamán et al. [19] synthesized helical MWCNTs from acetylene at 700 °C using the same catalyst. The different carbon sources and reaction temperatures led to the different morphologies of CNTs. In addition, the single-walled CNTs (SWCNTs) was firstly synthesized from CO at 1200 °C by Dai et al. [20]. Consequently, low reaction temperature (300–800 °C) tends to generate MWCNTs, whereas high reaction temperature (600–1150 °C) tends to generate CNTs with a small number of walls [8,21], such as double-walled CNTs and triple-walled CNTs [2]. Besides, other parameters such as reaction time, the reaction atmosphere, water, oxygen and catalysts are significant factors on the formation of CNTs [22–28]. Yao et al. [29] proposed that the catalyst composition and operational parameters significantly affected the production of CNTs from real-world waste plastics. Different catalyst temperatures and steam to plastic ratios could be adjusted to optimize the yield of CNTs [30]. Therefore, these parameters are key points to determine a feasible approach for designing high quality CNTs.

Synthesis of CNTs from waste organics especially waste plastics has been proposed in recent years. Alireza et al. [31] proposed the idea of using plastic polymers as the carbonaceous feed of CNT production. The production of MWCNTs from plastic polymers is satisfactorily achievable to meet the industrial development of CNTs. Yao et al. [29] further proposed the co-production of hydrogen and CNTs from real-world waste plastics. Recently, waste cooking oil (WCO) has attracted our attention and interest, since WCO contains abundant carbon atoms and hydrogen atoms, and its large annual amount was higher than 5 million tons [32]. Therefore, WCO is a potential carbon source for the synthesis of CNTs and a potential hydrogen source for H₂ production. In our previous work, WCO and ethyl acetate (a model component of WCO) have been investigated for producing H₂ via autothermal reforming (ATR) over the Ni₃La₇O_y/Al₂O₃ catalyst [33]. Particularly, obvious filamentous carbon was observed in the surface of the used catalyst. Besides, Shen et al. [34] also found that the catalytic decomposition of methane over Ni-Cu catalyst co-produced hydrogen and carbon. Therefore, the discovery stimulated the idea of co-producing CNTs and H₂ from WCO and ethyl acetate.

In this work, ethyl acetate and WCO were selected as new carbon sources for controllably synthesizing CNTs via ATR over the Ni₃La₇O_y/Al₂O₃ catalyst for the first time. The parameters such as reaction temperature, reaction time, concentrations of reactants (EA, O₂ and H₂O) were studied to design a feasible approach. The growth mechanism of CNTs in this work was discussed.

2. Experimental section

2.1. Synthetic methods

2.1.1. Catalyst preparation

The Ni₃La₇O_y/Al₂O₃ catalyst was prepared by the impregnation method. Typically, the Ni(NO₃)₂·6H₂O (AR, 0.64 g) and La(NO₃)₃·nH₂O

(AR, 2.22 g) with Ni/La molar ratio of 3:7 were added into a beaker and then dissolved by deionized water (5 g) to form the precursor solution. After that, the Al₂O₃ (CP, 10 g) was added into the precursor solution. After sufficient impregnation, the obtained material was dried at 80 °C for 6 h, and then calcined at 700 °C for 2 h. The obtained catalyst was named as Ni₃La₇O_y/Al₂O₃.

2.1.2. Co-production of CNTs and H₂ from ethyl acetate via ATR

Synthesis of CNTs and H₂ from ethyl acetate and water via ATR was performed in a fixed bed reactor using 3 g catalyst at the GHSV of 20,000 h⁻¹. The fixed bed reactor is a stainless steel tube with inner diameter of 8 mm, external diameter of 12 mm, length of 800 mm and two thermocouples fixed in both sides of the catalyst layer to measure the temperatures before and after reaction. Ethyl acetate (6 ml/h) and distilled water (4 ml/h) were fed by HPLC pumps to control the flow velocity, while oxygen (10 ml/min) and nitrogen (90 ml/min) were controlled by mass flow controllers. The liquids and gases were mixed in a preheating chamber for gasification at 200 °C before entering the fixed-bed reactor. The gasified reactants entered into the reactor, interacted with the catalyst, and then the hydrogen and CNTs were produced at different reaction temperatures such as 500, 600, 700 and 800 °C. After the ATR reaction, the feed of reactants was stopped, instead the reactor was filled by N₂ for protecting the CNTs until decreasing the temperature of the reactor to the room temperature. The CNTs samples were obtained and carefully preserved for further tests. The pure CNTs were obtained by dissolving catalyst of the CNTs samples at 60 °C for 3 h using HCl. CNTs was filtered by nano-film with apertures of 45 nm, washed by distilled water and dried at 100 °C.

The obtained samples are named as CNTs-T-t-E_x-H_y-O_z, where T is reaction temperature, t is reaction time, E is the amount of ethyl acetate, H is the amount of H₂O and O is the amount of O₂. x, y and z are values of each reactants. Sample generated with 600 °C, 6 h, 6 ml/h ethyl acetate, 4 ml/h H₂O and 10 ml/min O₂ was named as CNTs-600-6-E6-H4-O10.

The amount of synthesized H₂ was measured online by gas chromatograph (GC-2014). The gases were tested by a TCD detector equipped with a TDX-01 column.

Synthesis of CNTs from real WCO

CNTs produced from real WCO were conducted under the reaction condition: 6 ml/h WCO, distilled water (4 ml/h), oxygen (10 ml/min) and nitrogen (90 ml/min). The ATR reaction was performed at 800 °C for 6 h. The treatment of the products was similar to that of the samples produced from ethyl acetate.

2.2. Characterizations

Powder X-ray diffraction (XRD) patterns were carried out on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The 2 θ scans covered the range 10–80° (5°/min), and the accelerating voltage and applying current were 40 kV and 30 mA, respectively.

Raman experiments were performed on a Renishaw inVia 2000 Raman microscope using the Ar⁺ 514.5 nm line as the excitation radiation at a power of 25 mW.

The micro-structure in the surface of the catalysts was measured by FESEM (ZEISS Ultra 55 field-emission scanning electron microscope).

The TEM and HRTEM graphs of formed CNTs was measured by a 200 kV Joel 2010F trans-mission electron microscope (TEM).

The AXIS ULTRA DLD instrument was used for XPS analysis, and monochromatic Al-K α radiation was used as the excitation source. After complete removal of moisture from the catalysts by drying at 100 °C for 24 h, the catalysts were analyzed without surface sputtering or etching so that the degree of vacuum in the XPS equipment was maintained at 10⁻⁷ Pa.

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